TABLE IV

Relative Oxidation Rate (ROR) of Emulsion with Maillard Products

Sample[a] (hr)	ROR[b]
4	0.82
8	0.84
17	0.77
24	0.76
Lysine/no dextrose	1.04

[a] Maillard reactions between lysine and dextrose in water solution at 60 C for the time indicated. Applied at 1% level calculated on lysine basis.

[b] Relative to control (amino-acid-free) emulsion which after 25 days at RT had absorbed 148.2 meq O_2/Kg of oil.

gradually grew darker with time. It appears from the table that there is virtually no difference in the oxidation rates of these emulsions and they are only slightly more stable than control emulsions with unreacted lysine and without amino acid.

These results are preliminary. More work should be done in this area to understand better the influence of Maillard products on the autoxidation of oils, and to evaluate the potential of these active components for commercial use.

REFERENCES

1. Marcuse, R., JAOCS 39:97 (1962).
2. Marcuse, R., Fette Seifen Anstrichtsm. 63:940 (1961).
3. Sliwiok, J., and J. Siechowski, Riv. Ital. Sost. Grasse 1970:47.
4. Farag, R.S., S.A. Osman, S.A.S. Hallabo and A.A. Nasr, JAOCS 55:703 (1978).
5. Farag, R.S., S.A. Osman, S.A.S. Hallabo, A.M. Girgies and A.A. Nasr, Ibid. 55:708 (1978).
6. Farag, R.S., S.A. Osman, S.A.S. Hallabo and A.A. Nasr, Ibid. 55:613 (1978).
7. Sims, R.J., J.A. Fioriti and J. Trumbetas, Ibid. 56:742 (1979).
8. Bishov, S.J., and A.S. Henick, JAOCS 43:477 (1966).
9. Fioriti, J.A., M.J. Kanuk and R.J. Sims, Ibid. 51:219 (1974).
10. Trumbetas, J.F., J.A. Fioriti andR.J. Sims, Ibid. 54:433 (1977).
11. Trumbetas, J.F., J.A. Fioriti and R.J. Sims, Ibid. 55:248 (1978).
12. Official Methods of Analysis, 4th Edition, Assoc. Off. Anal. Chem., 1975, Method 31.069-071, p. 577.
13. Sims, R.J., and J.A. Fioriti, Ibid. 54:4 (1977).
14. Saleeb, F.Z., C.J. Cante, T.J. Streckfus and J.R. Frost, JAOCS 52:208 (1975).
15. Rhee, C., and D.H. Kim, J. Food Sci. 40:460 (1975).

[Received January 18, 1980]

Determination of Phosphorus in Oils Using Oxygen Bomb Ashing

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ABSTRACT

A fast method for phosphorus determination in an oil matrix is described. The principle of the method is similar to that of the AOCS method, but the ashing of the oil is accelerated using an oxygen bomb. In addition, a rapid molybdovanadate reagent is used for colorimetry rather than the molybdenum blue reagents specified in the AOCS method. Agreement with the air ashing procedure averages less than 5% difference above 10 μg/g. The detection limit is in the order of 1-2 μg/g.

INTRODUCTION

The official American Oil Chemists' Society (AOCS) method (1) for the determination of phosphorus in oil has been in use for many years. The colorimetric measurement of phosphate as molybdenum blue is often replaced by the more stable yellow molybdovanadate phosphate complex (2-5), which is more tolerant to pH variations and has fewer anionic interferences. Also, the molybdovanadate procedure is faster and has fewer steps. Even though the sensitivity is not quite as high as that of the molybdenum blue procedure, it is adequate for most applications.

The hot plate/muffle furnace combination is still the most commonly used ashing procedure. The major disadvantage of this method is that it is time-consuming. Attempts to speed up the ashing by wet digestion with nitric and perchloric acids (6) are not popular because of the hazards of heating these acids in the presence of oil.

Physical methods offer a possible way to achieve faster analysis. These are being investigated by several researchers. Prevot (7, 8) obtained sensitivity in the 1 μg/g range using atomic absorption spectrophotometry with graphite furnace atomization. Belcher and coworkers (9) developed a technique called Molecular Emission Cavity Analysis (MECA) to study molecular emission using a special sample chamber. Both of these methods are relatively fast because they require little or no sample preparation. But, they are not developed enough for routine use as yet.

Since ashing of the oil is the most time-consuming part of the official AOCS method, any improvement here would be the most beneficial in terms of speed of analysis. An oxygen bomb can be used to greatly accelerate the ashing of the oil (10). The sample is ignited in a pressure vessel filled with oxygen to 22-25 atmospheres by melting a thin wire with an electric current. The oxygen bomb reduces the ashing time from one day on a hot plate and muffle furnace to ca. 15 min.

The combination of the oxygen bomb and the molybdovanadate reagent has been found to provide a simple, rapid, method for the determination of phosphorus in oil.

EXPERIMENTAL

Apparatus

The oxygen bomb apparatus used in this study was the Parr Instrument Co. Model 1901. The stainless steel capsules supplied with the apparatus were used as sample holders. Any spectrophotometer capable of measuring absorbance to 0.001 units is suitable. In this report, a CARY 118 was used.

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Reagents and Solutions

The ashing aid was reagent grade zinc oxide (ZnO). Dilute nitric acid was prepared by adding 1 vol concentrated nitric acid (70%) to 9 vol distilled water. A standard phosphate stock solution containing 2500 μg/ml was prepared by dissolving 10.984 g of reagent-grade anhydrous potassium dihydrogen phosphate ([KH_2PO_4] dried at 105 C for 4 h) in distilled water and diluting to 1 ℓ. Diluting 5 ml of the stock standard to 500 ml gave a working standard containing 25 μg/ml. The molybdovanadate reagent (color reagent) was prepared in 3 steps. First, 15 g of reagent-grade ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was dissolved in 200 ml distilled water with mild heating. Then, 1 g of reagent-grade ammonium metavanadate, NH_4VO_3, was separately dissolved in 200 ml distilled water with mild heating. This solution was cooled before slowly adding 200 ml perchloric acid (70%), then mixed well and cooled to room temperature. The normal precautions for handling perchloric acid if it is spilled should be followed. The molybdate solution was slowly added to the vanadate solution with frequent mixing. The combined solution was diluted to 1ℓ.

Procedure

An oil sample was weighed to the nearest 0.1 mg into a dry, clean capsule. The stainless steel capsules were cleaned by heating at 500 C, rinsing with dilute nitric acid followed by distilled water, then drying. The sample size was 0.4 g if phosphorus was above 100 μg/g, and 0.8 g if less than 100 μg/g. Not more than 0.8 g of oil can be ashed at one time or the pressure limits of the oxygen bomb may be exceeded. Tongs were used to handle the capsule. Zinc oxide (0.02-0.1 g) was added as an ashing aid to ensure complete combustion. The capsule was heated on a hot plate briefly to disperse the ZnO. A 10-cm length of fuse wire (supplied with the bomb) was attached to the electrodes as shown in the instruction manual for the oxygen bomb, bending the wire so that it hangs in a U-shape. The capsule was placed on the loop electrode and the fuse wire was positioned ca. 1-3 mm above the oil. Two ml of distilled water were added to the bottom of the bomb. The bomb was closed and then filled with oxygen to 22-25 atmospheres. After ignition, the bomb was cooled in a container of cold water. The pressure in the bomb was released slowly before opening. A fine jet of distilled water was used to rinse the outside of the capsule before it was removed from the bomb. Rinsewater must be used sparingly to avoid overfilling the 25-ml flask. The cover and electrodes were rinsed, allowing the washings to fall into the bomb. One ml of dilute nitric acid was added to the capsule to dissolve the residue. The solution was filtered through Whatman #1 paper into a 25-ml volumetric flask along with the rinsing from the capsule and the bomb. The flask was filled to volume with distilled water.

The color development step is very simple. For oils with phosphorus levels above 100 μg/g, a 5-ml aliquot of the sample solution was pipetted into a 25-ml volumetric flask. Five ml of color reagent were added and the flask was filled to volume with distilled water. The color was allowed to develop for 10 min, then the absorbance was measured at 400 nm. For oils below 100 μg/g, 5 ml of color reagent was added to a dry 25-ml volumetric flask. The flask was then filled to volume with the sample solution, in essence, a 20-ml aliquot. The absorbance was measured as already described.

A calibration curve of absorbance vs μg phosphorus was generated by measuring the absorbances for 3 different amounts of phosphorus. Aliquots of 0, 1 and 3 ml of the working standard solution were pipetted into separate 25-ml flasks. Five ml of color reagent were added to each flask. The solutions were diluted to volume and the absorbance measured as described. These standards correspond to 0, 25 and 75 μg of phosphorus. Typical absorbance values using a 1-cm path length cuvette for 0 and 75 μg are 0.028 and 0.290, respectively. Beer's law is obeyed up to ca. 100 μg. The amount of phosphorus in the aliquot from an unknown sample was either read from the graph or calculated from the slope and intercept of the straight line best fitting the 3 standard points. If the phosphorus in the aliquot is Y μg (after correcting for the ashing blank), the concentration (μg/g) in the oil is 25 Y/VW, where V is the aliquot volume and W is the weight of oil.

An ashing blank was carried through the entire procedure. The blank correction, which is dependent on the purity of the reagents if contamination from glassware and the lab environment is controlled, was fairly constant, averaging 1 μg phosphorus for a 20-ml aliquot. Nitric acid is used instead of hydrochloric acid to dissolve the ash because HCl leaches phosphorus from the stainless steel capsules. At the detection limit, the blank may contribute up to 50% of the total phosphorus present.

For the air ashing procedure, 1-3 g of oil and 0.1 g of ZnO were weighed into porcelain crucibles. The oils were ashed on a hot plate until black, then placed in a muffle furnace at 500 C overnight. The residue was dissolved with 2 ml dilute nitric acid, filtered through Whatman #1 paper into a 25-ml volumetric flask and then filled to volume. A suitable aliquot was pipetted into a 25-ml flask and carried through the same color development procedure as with the oxygen bomb.

RESULTS AND DISCUSSION

To confirm that the molybdovanadate reagent gives comparable results to the AOCS molybdenum blue procedure (1), several oil samples were analyzed using both methods. Equal aliquots of the same dissolved ash solution were analyzed to avoid the small errors contributed by the weighing and ashing steps. The results, tabulated in Table I, are in good agreement.

The results for the oxygen bomb and air ashing comparison using the molybdovanadate reagent for both procedures are tabulated in Table II. These oils were analyzed over a period of nine months using several batches of color reagent, demonstrating that consistent results can be obtained on a long-term basis. Above 10 μg/g, the difference between the 2 methods averages 3.8% for this set of data. Similar agreement is obtained for current routine analyses. Below 10 μg/g, the agreement is usually within 2 μg/g. The lower limit of detection is between 1-2 μg/g.

The agreement between the oxygen bomb and the air ashing procedures is good. However, the outstanding feature of the bomb procedure is its speed of analysis. One sample of oil can be ashed and made ready for the colorimetric procedure in ca. 15 min. In process control applications, the analysis of one or 2 samples in under 1 hr can be very

TABLE I

Comparison between Molybdenum Blue and Molybdovanadate Reatent

	Phosphorus (μg/g)	
Oil	Molybdenum blue	Molybdovanadate
Crude soybean	134	132
Refined rapeseed	5.2	7.2
Crude rapeseed	228	225
Blend of several oils	28	31
Blend of several oils	84	80

TABLE II

Comparison between Air and Oxygen Bomb Ashing

	Phosphorus (μg/g)		
Oil	Air ashing	Oxygen bomb	Difference (%)
Soybean, crude	112	118	+5.4
Rapeseed, crude	231	229	-0.9
Corn, crude	880	857	-2.6
Blend of several oils	13	14	+7.7
↓	24	25	+4.2
	38	40	+5.3
Rapeseed, crude	245	246	+0.4
Soybean, crude	130	123	-5.4
Rapeseed, crude	242	237	-2.1
Corn, refined	6.6	5.9	
Corn, refined	3.5	4.3	
Soybean, refined	5.4	6.2	
↓	1.2	2.1	
	2.8	4.1	
	8.6	8.4	
Blend of several oils	8.0	7.2	

useful. If more than ca. 15 samples are to be analyzed, the analysis time approaches that for the air ashing. The reason is that the oxygen bomb ashes the samples sequentially, whereas the hot plate ashes the samples concurrently. When the analysis times for a group of samples are similar, the air ashing procedure is more economical because the analyst can be doing other work while the oil is ashing. The oxygen bomb procedure requires the full attention of the analyst.

Both the oxygen bomb and the air ashing methods described here are rather insensitive to variations of several factors. The presence of ZnO is essential for complete combustion of the oil. However, the actual amount of ZnO is ot important as long as it exceeds 0.02 g. The volume of ilute nitric acid that is used to dissolve the ash is not ritical up to 6 ml. Exceeding this volume decreases the absorbance. The latitude in the acid concentration shows that accurate pH control is unnecessary.

The oxygen bomb method has been used for over 1 year in this laboratory and has been found suitable for fast, accurate, phosphorus determinations in oils. When the number of samples at any one time is large, the air ashing procedure described in this report works equally well.

ACKNOWLEDGMENT

The technical help and ideas from Jennifer Zuk and Carrol H. Perrin, Research Centre, Canada Packers Inc., are gratefully acknowledged.

REFERENCES

1. "Official and Tentative Methods of the American Oil Chemists' Society," 3rd Edition, AOCS, Champaign, IL, 1973, Method Ca 12-55.
2. Racicot, E.L., Anal. Chem. 23:1873 (1951).
3. Quinlin, K.P., and M.A. DeSesa, Ibid. 27:1626 (1955).
4. Hunt, R.W., Jr., and L.G. Hargis, Ibid. 49:779 (1977).
5. "AOAC Methods," 12th Edition, Association of Official Analytical Chemists, Washington, DC, 1975, p. 11.
6. Harris, W.D., and P. Popat, JAOCS 31:124 (1954).
7. Prevot, A, and M. Gente-Jauniaux, Revue Fr. Corps Gras 24:493 (1977).
8. Gente-Jauniaux, M., and A. Prevot, Ibid. 26:325 (1979).
9. Belcher, R., S.L. Bogdanski and A. Townshend, Anal. Chem. Acta 67:1 (1973).
10. Piercy, G.T., E.K. Plant and M.C. Rogers, Ind. Eng. Chem. Anal. Ed. 12:165 (1940).

[Received May 6, 1980]

Rapid Instrumental Technique for the Analysis of Volatiles in Salad Dressing[1]

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ABSTRACT

A simple, rapid, efficient procedure for analyzing the volatile components in salad dressings is described. A unique inlet system, used in conjunction with gas chromatography and mass spectrometry, provides an objective, tangible profile of volatiles characteristic of the product. The individual components may be identified to qualify more effectively the odor and flavor quality of the specimen.

INTRODUCTION

The detection and identification of volatiles that contribute to food flavor quality have recently become the object of extensive research. Organoleptic methods of assessing food flavor quality, although reasonably effective, are complex and costly (1-3) and are ultimately limited by the taster's judgment. In 1971, Dupuy et al. (4) described a novel, direct, gas chromatography (GC) procedure for determining volatiles in vegetable oils. The method was further refined, and in 1973 (5) it was applied to the examination of oils and shortenings.

Other workers, using variations of this technique (6,7), found excellent correlation between taste panel flavor scores of oils and instrumental data. Although high-moisture foods are inherently unsuitable for combined GC-mass spectrometry (MS) determinations, Legendre et al. (8) have described a unique, versatile inlet system that accommodates both high- and low-moisture foods for GC-MS analysis. This work reports the use of this novel inlet system for the analysis of changes that occur in a salad dressing during storage.

EXPERIMENTAL PROCEDURES

The materials, instruments, GC and MS conditions used in this study have been detailed previously (8). For sample preparation, a 3-3/8 in. length of 3/8 in. od borosilicate glass tubing was packed at one end with ca. 200 mg of glass wool, and 300 mg of potassium carbonate was added. The potassium carbonate functions as a built-in clean-up column

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[1] Presented at the AOCS Meeting, San Francisco, April 1979.

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